

## **Methods for Evaluation of Transmittance Minima in Wavenumber Standards**

### **Spectra: a Comparison and Analysis**

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#### Introduction and Description of the Parameters.

Calibration of the wavenumber scale is an important component to insuring the measurement accuracy of FT-IR spectrometers. The calibration process involves a number of important steps from measurement of standard gas lines or absorption bands, to the analysis of the measured spectra to obtain wavenumber values for comparison with the standard values. This last step can contribute error and uncertainty if not performed properly. In 1995 NIST conducted an intercomparison of band analysis software in which a number of FT Manufacturers participated. Even though all participants applied their software on identical polystyrene spectra data files, typically the variation in results was approximately  $1\text{ cm}^{-1}$  (excluding the worst case methods). This has led us to investigate various aspects of the band analysis process and to develop new methods as well. In this paper we examine key parameters of the spectral analysis process and discover how they can affect the result for the case of NIST's SRM (standard reference material) 1921a polystyrene wavenumber standard. We include two methods of band analysis recently developed at NIST for use on standard spectra. These are designed for locating band minima and to complement the currently used centroid method (with band

fractions 0.5 and 0.1) for SRMs 1921a and 2035, and to replace the bisecting method used for SRM 2034.

The parameters we investigate in this study are involved in (a) the conversion of the directly measured interferogram obtained by a FT-IR spectrometer into spectra, and (b) the analysis of the transmittance spectra obtained from ratios of the standard sample and reference measurements. In (a) the effects of (1) spectral resolution, (2) apodization function and (3) zero-filling level, are examined, and in (b) the effects of the methods used for the band minima determination are compared.

The study is performed on a data set consisting of 72 measurements of 12 samples of NIST SRM 1921a. They were measured sequentially in 6 cycles under identical conditions in vacuum at  $0.5\text{ cm}^{-1}$  resolution with the FTIR set up with SiC source, DTGS detector, and KBr beamsplitter. Measurement times were approximately 20 minutes for sample and reference measurements. To obtain lower resolution results, the raw interferograms were truncated appropriately before processing. Except for the data spacing study, all interferograms were zero-filled to high resolution ( $0.013\text{ cm}^{-1}$ ) to eliminate that source of error (see data spacing results discussion). 13 polystyrene absorption bands calibrated for SRM 1921a were evaluated in this study and are referred to subsequently in the text by sequence number: (1) 540, (2) 840 (3) 906, (4) 1028, (5) 1069, (6) 1154, (7) 1583, (8) 1601 (9) 2850, (10) 3001, (11) 3026, (12) 3060 and (13)  $3082\text{ cm}^{-1}$ .

Specific parameter values for the analysis were selected to span the range for which the standard might be used. Spectra were analyzed for (1) spectral resolution parameter values of 0.5, 1.0, 2.0 and 4.0  $\text{cm}^{-1}$ . No difference from the 0.5  $\text{cm}^{-1}$  results are expected or have been seen for higher resolution spectra, since all the calibrated bands are fully resolved at 0.5  $\text{cm}^{-1}$ . Beyond 4.0  $\text{cm}^{-1}$ , lower resolution spectra will contain several significantly distorted bands. The (2) apodization functions used in the Fourier transform process were Boxcar and Hamming (AKA Happ-Genzel). Again these represent the extremes: from no apodization (Boxcar) to approximately triangular (Hamming). Results for all other commonly used apodization functions should lie within the range of the results seen here. The (3) wavenumber axis spacing of the spectral data (from zero-filling) was varied from 0.013  $\text{cm}^{-1}$  to 1.0  $\text{cm}^{-1}$ . Larger values are also common for the user for lower resolution measurements (e.g. 4.0  $\text{cm}^{-1}$ ). However, as can be seen from the results below, values of data spacing greater than 1.0  $\text{cm}^{-1}$  can lead to significant errors and should be avoided, at least with the use of 1921a. Finally, (4) five different methods and two additional variations for determining the location of absorption band minima are compared: extrapolated centroid (EC), enhanced computational bisecting (EB), quadratic fit using 30 points (QD), cubic spline fit using 4 points (CS), and centroid using 3 points, with no smoothing (C0), 49 point smoothing (C49), and 99 point smoothing (C99).

The extrapolated centroid method (EC) was developed by NIST to be able to provide users with calibrated band minima locations for its wavenumber standards. NIST currently uses the centroid method (C) with band fractions of 0.5 and 0.1 for its mid- and near-infrared wavenumber standards SRMs 1921a and 2035, respectively. The NIST

centroid method has very good reproducibility due to its band averaging nature. However, the band values obtained are not directly comparable to the band minima locations. But the EC (and EB) method values can be directly compared with those obtained by other methods, as demonstrated in this paper. The EC method consists of calculating a series of centroid values for different band fractions ranging from 0.5 to 0.05 in steps of 0.05 (or other range such as 0.10 to 0.01 in 0.01 steps). An extrapolation is then performed on the series of centroid values to a value for '0' band fraction (band minimum) using a quadratic or cubic fit. In addition, for the results in this paper, the six values obtained for each sample were averaged and the corresponding standard deviation values were used in a chi-squared weighting applied to the curve fits.

The enhanced computational bisecting method (EB) was developed as a computed replacement to the manual graphical 'bisecting' method used at NIST for the near-infrared reflection and ultraviolet-visible wavelength standards SRMs 1920 and 2034. The EB method consists of obtaining a set of values from fractions of the band ranging from 0.50 to 0.05. For each band fraction, values are obtained that bisect the band. These values are then fit with a quadratic or cubic function. The intersection of the curve fit of the bisecting points with the spectrum of the band is the value obtained for the band minimum. In addition, a quadratic fit is made to the bottom of the band for determination of the intersection with the curve fit to the bisected data.

## Results and Discussion.

### Resolution

For all calibrated polystyrene bands, using Boxcar apodization, no significant effect on band location is seen for resolutions from  $0.5\text{ cm}^{-1}$  up to  $4\text{ cm}^{-1}$ . When comparing the mean values of all 72 measurements, the maximum difference due to resolution for all 13 bands and all methods is  $0.09\text{ cm}^{-1}$ . For 11 of the 13 bands, for the EC and EB methods, the maximum difference is  $0.01\text{ cm}^{-1}$ . Beyond  $4\text{ cm}^{-1}$ , location shifts are observed for the narrow bands. Also, for  $4\text{ cm}^{-1}$  resolution, use of Hamming apodization results in position shifts of narrow lines due to the decreased effective resolution. As discussed below, for low resolution measurements it is important to zero-fill or interpolate to obtain sufficiently small data spacing (here  $0.013\text{ cm}^{-1}$  is used).

### Apodization

The main effect of apodization is a change in effective resolution. Hence for narrow bands, strong apodization such as Hamming can cause an apparent shift. For polystyrene, Hamming can be used for resolutions of  $2\text{ cm}^{-1}$  or less. This should also be true for similar functions such as Triangle. For sufficiently high resolution no significant effects can be seen related to apodization for all methods used. When comparing the mean values of all 72 measurements, the maximum difference due to apodization results for all 13 bands and all methods is  $0.10\text{ cm}^{-1}$ . For the EC, EB, and C99 methods, the maximum difference is  $0.02\text{ cm}^{-1}$ .

### Data Spacing

The data interval of the spectrum can play an important role in how accurately a band minimum can be determined. Analyses of the effects of finite data spacing (interval) on the EC and centroid with 0.5 band fraction methods have been performed for all 13 polystyrene bands. [Although not a minimum locating method, the centroid (0.5 band fraction) method is used for NIST standards and exhibits a clear dependence on data spacing.] Factors that affect the data spacing error include the band's width (error inversely proportional to width) and asymmetry (larger error with increased asymmetry). For the centroid method, the maximum error for the 13 bands varies from 0.03 to 0.4  $\text{cm}^{-1}$  at 1  $\text{cm}^{-1}$  data spacing. At 0.4  $\text{cm}^{-1}$  data spacing the maximum error is less than 0.05  $\text{cm}^{-1}$  for all bands, and for 0.2  $\text{cm}^{-1}$  spacing the error is less than 0.01  $\text{cm}^{-1}$ . For the EC method, the maximum error for 12 of the 13 bands at 0.4  $\text{cm}^{-1}$  spacing range from 0.01  $\text{cm}^{-1}$  to 0.2  $\text{cm}^{-1}$ , whereas for 0.2  $\text{cm}^{-1}$  spacing, the error for all bands is less than 0.05  $\text{cm}^{-1}$ , and for 0.1  $\text{cm}^{-1}$  less than 0.01  $\text{cm}^{-1}$ . Hence zero filling can be used to reduce the error contribution from finite data spacing to any desired level. The dependence of the maximum error on data spacing may be quantitatively but not qualitatively different for other methods.

### Methods Comparison

For the means of the band locations for the entire set of 72 spectra, all seven methods are found to be in reasonable agreement as shown in Figure 1. Hence the EC and EB methods are able to obtain band minima values that are consistent with other commonly used methods. Large amounts of smoothing can result in some discrepancies (C99). The

standard deviation of the means, shown in Figure 2, reveal that agreement for individual spectra is less consistent and depends strongly on the relative noise level in the spectrum. The  $0.5\text{ cm}^{-1}$  results show considerably larger standard deviations for the methods using fewer points of the band (QD, CS, C0, and C49) as compared to those methods using large numbers of points (EC, EB & C99). In contrast, the analogous data for  $4\text{ cm}^{-1}$  resolution have nearly identical standard deviations for all methods.

### Discussion and Conclusions

All parameters studied (apodization, resolution, band evaluation method, and data spacing) are important in the determination of the band locations and in particular NIST's wavenumber standards. Two new NIST methods (EC and EB) combine good reproducibility (of the centroid 0.5 method) with the ability to locate band minima accurately (agreement with QD, CS, and C methods). Every method used can produce reasonable results, provided its parameters are suitably adjusted (sometimes differently for each band and resolution). Parameters for each method were not necessarily optimized for each case in this study. More details of the methods and analyses can be found in References 1 and 2

### References

1. C. Zhu and L. M. Hanssen, "Absorption line evaluation methods for wavelength standards," Proc. SPIE 3425, 111-118 (1998).
2. C. Zhu and L. M. Hanssen, "Study of polystyrene wavenumber standard for infrared spectrophotometry," Proc. SPIE 4103, 62-68 (2000).

Figure Captions:

Figure 1. Comparison of 7 methods for band minima location. The mean wavenumber locations from 72 spectra of 12 polystyrene standard samples are compared. The difference between each method's result and the common mean is plotted for all 13 calibrated bands. Each method has an associated curve whose label is defined in the text.

Figure 2. Comparison of 7 methods. The standard deviations of the associated means shown in Figure 1.



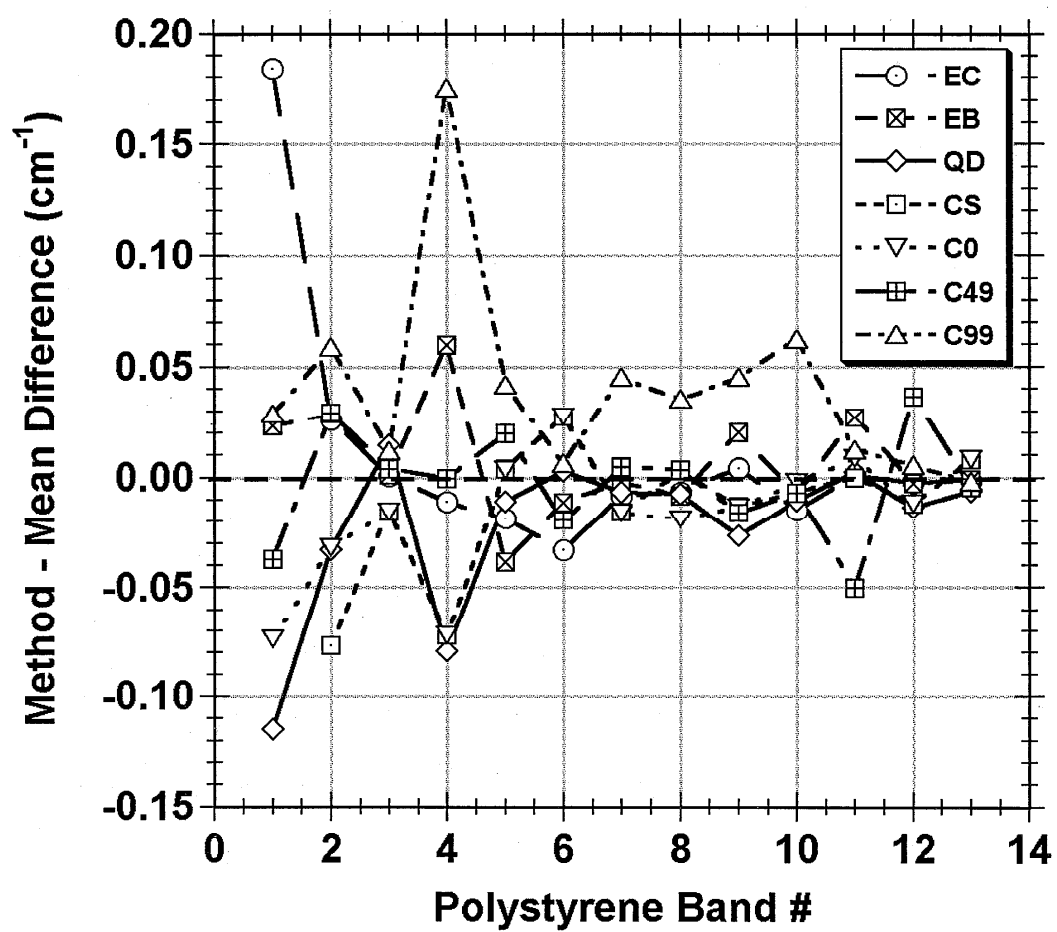


Figure 1.

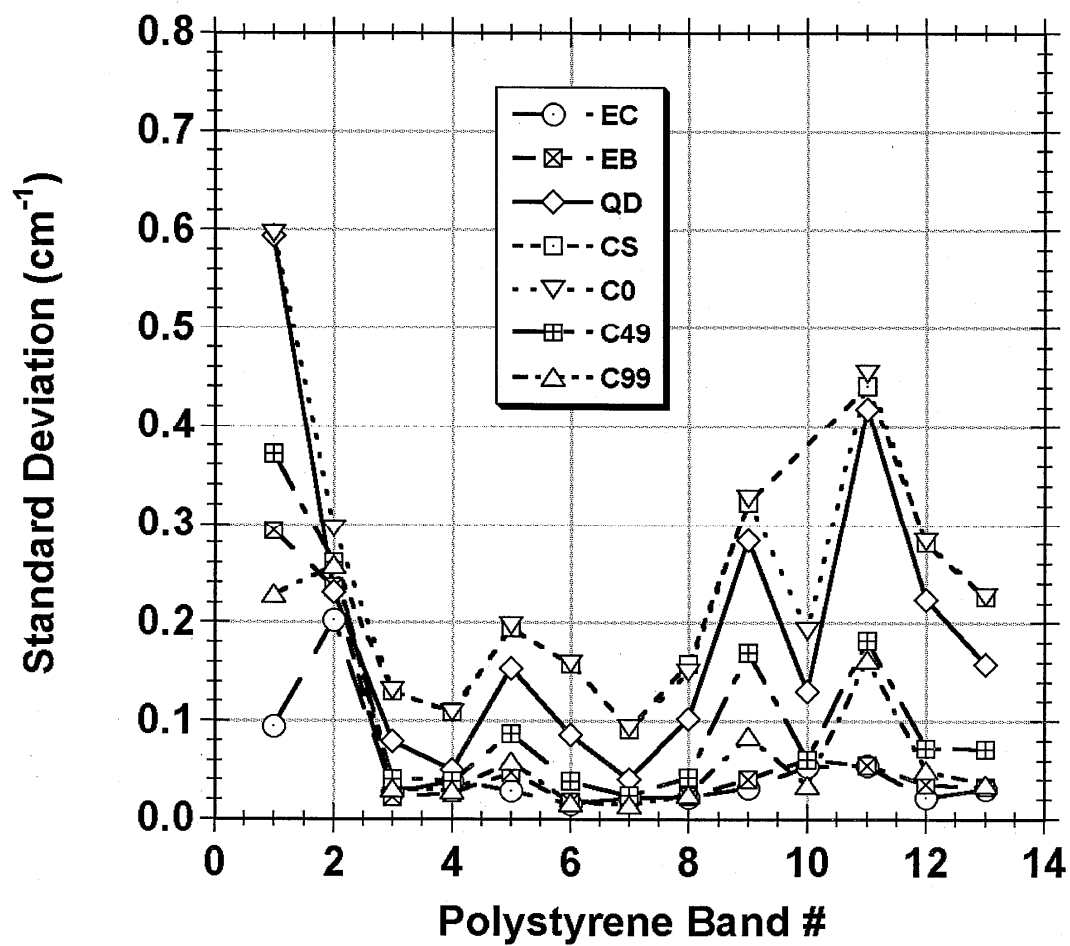


Figure 2.